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(21) International Application Number: PCT/US99/10173 (22) International Filing Date: 10 May 1999 (10.05.99) (30) Priority Data: 09/075,586 11 May 1998 (11.05.98) US (71) Applicant: DURACELL INC. [US/US]; Berkshire Corporate Park, Bethel, CT 06801 (US). (72) Inventors: MOSES, Peter, R.; 61 Kendall Pond Road, Windham, NH 03087 (US). BOWDEN, William, L.; 28 Cathedral Circle, Nashua, NH 03063 (US). ILTCHEV, Nikolay; 1 Old Colony Road, Norfolk, MA 02156 (US). BRANDT, Klaus; 50 Summit Road, Wellesley, MA 02181 (US). (74) Agents: HANDELMAN, Joseph, H.; Ladas & Parry, 26 West 61st Street, New York, NY 10023 (US) et al.		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: LITHIATED MANGANESE OXIDE (57) Abstract A lithiated manganese oxide for use in primary lithium cells is described. The lithiated manganese oxide can be prepared by exposure to a lithium source under conditions that result in the formation of a modified manganese oxide phase. When the modified phase is used in a primary lithium cell, the operating voltage of an electrochemical cell containing the lithiated manganese oxide increases relative to the operating voltage of a cell containing a manganese dioxide that is not exposed to the lithium source.		

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LITHIATED MANGANESE OXIDE

This invention relates to lithium electrochemical cells.

A battery includes one or more galvanic cells (i.e., cells that produce a direct current of electricity) in a finished package. Cells of this type generally contain two electrodes separated by a liquid capable of transporting ions, called an electrolyte. Typical electrolytes include liquid organic electrolyte or a polymeric electrolyte. The cell produces electricity from chemical reactions through oxidation at one electrode, commonly referred to as the negative electrode, and reduction at the other electrode, commonly referred to as the positive electrode. Completion of an electronically conducting circuit including the negative and positive electrodes allows ion transport across the cell and discharges the battery. A primary battery is meant to be discharged to exhaustion once, and then discarded. A rechargeable battery can be charged and discharged multiple times.

An example of a primary battery is a primary lithium cell. A lithium electrochemical cell is a galvanic cell using lithium, a lithium alloy or other lithium containing material as one electrode in the cell. The other electrode of the cell can include, for example; a metal oxide, such as a manganese dioxide (e.g., $\gamma,\beta\text{-MnO}_2$). The metal oxide used in the electrode can be processed prior to use in a lithium battery. Generally, manganese dioxide can be prepared by chemical methods or electrochemical methods. The resulting materials are known as chemically produced manganese dioxide (CMD) and electrochemically produced (e.g., electrolytic) manganese dioxide (EMD), respectively. A rechargeable battery, such as a lithium ion battery, can include a lithiated carbon electrode.

Manganese dioxide-based lithium cells are described, for example, in Ikeda, et al. "Manganese Dioxide as Cathodes for Lithium Batteries," in Manganese Dioxide Symposium, Vol. 1, The Electrochemical Society, Cleveland Section, 1975, p. 384-401, incorporated herein by reference.

The invention relates to a lithiated manganese oxide for use in electrochemical cells. The lithiated manganese oxide can be prepared by exposure to a lithium source under conditions that results in the formation of a modified manganese oxide phase. When the modified phase is used in a primary lithium cell, the operating voltage of an electrochemical cell containing the lithiated manganese

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oxide increases relative to the operating voltage of a cell containing a manganese dioxide that is not exposed to the lithium source.

In one aspect, the invention features a manganese oxide composition that includes a lithiated manganese oxide. The lithiated manganese oxide can have
5 an x-ray diffraction pattern including a 31 degree 2-Theta peak intensity of at least 35 percent and a 24 degree 2-Theta peak intensity of at least 35 percent.

In certain embodiments, the 31 degree 2-Theta peak intensity can be at least 36 percent. In other embodiments, the 24 degree 2-Theta peak intensity can be at least 38 percent. The 31 degree 2-Theta peak can be between 31 degrees and
10 32 degrees. The 24 degree 2-Theta peak can be between 24 degrees and 24.8 degrees.

The lithiated manganese oxide can have a discharge voltage of greater than 2.9V when tested in a CR 2430 coin cell (e.g, a primary lithium cell) at 1 mA/cm² continuous discharge at room temperature. It also can include greater than
15 about 0.7 weight percent (e.g., greater than 1.0 weight percent) lithium in MnO₂ and less than 59 weight percent Mn⁴⁺.

In another aspect, the invention features a method of preparing a lithiated manganese oxide.

In the method, a manganese oxide is placed in a liquid to provide a
20 suspension. The manganese oxide can be an electrochemically produced manganese dioxide (EMD). The liquid can be water.

A lithium salt is added to the suspension. The lithium salt can be lithium hydroxide. The pH of the suspension can be increased so that it is basic, such as to a pH greater than about 7, preferably greater than about 9, and more
25 preferably greater than about 11. For example, the pH of the suspension can be increased by adding a solution including lithium hydroxide to the suspension.

After adding the lithium salt, the liquid is removed to provide a solid. The liquid can be removed by filtering the suspension, centrifuging the suspension, or evaporating the liquid, or combinations thereof. The solid can be a sediment, a
30 particle or group of particles collected from a colloid, or a combination thereof.

The solid is heated to provide the lithiated manganese oxide. Heating can include raising the temperature of the solid to between about 350°C and 400°C.

In another aspect, the invention features an electrochemical cell including a first electrode and a second electrode. The second electrode can be a lithium electrode or a lithiated carbon electrode. The electrode can include a lithiated manganese oxide. The cell can have a discharge voltage of greater than
5 2.9V.

In another aspect, the invention features a method of manufacturing a lithium cell. The method includes preparing an electrode including a lithiated manganese oxide. The lithiated manganese oxide of the electrode can be prepared by placing a manganese oxide in a liquid to provide a suspension, adding a lithium
10 salt to the suspension to provide a suspension at a pH greater than about 11, removing the liquid from the suspension to provide a solid, and heating the solid to provide the lithiated manganese oxide.

The lithiated manganese oxide can have the following advantages. For example, the battery load voltage suppression can be improved by increasing the
15 lithium content of the MnO_2 . At the beginning of a heavy load low temperature discharge curve of lithium grade MnO_2 , the battery load voltage can be suppressed. Accordingly, the uses of the battery can be limited by the performance of the material, e.g., the suppressed load voltage does not meet the requirements for photographic camera applications. The lithium content of the manganese oxide can
20 be increased by carrying out the neutralization step to higher pH levels (e.g., greater than about 9). In the subsequent processing and drying of EMD to make it suitable for lithium batteries, the additional lithium can react with MnO_2 to form the lithiated manganese oxide. The lithiated manganese oxide can lead to an increase of the load voltage, especially at heavy discharge rates and at low temperatures.

25 Other features and advantages of the invention will be apparent from the description of the preferred embodiments and from the claims.

FIG. 1 is a graph depicting an x-ray diffraction pattern of a lithiated MnO_2 .

FIG. 2 is a graph depicting an x-ray diffraction pattern of a lithiated
30 MnO_2 .

FIG. 3 is a graph depicting the shifts in peak locations in the x-ray diffraction patterns of lithiated MnO_2 neutralized to various pH levels.

FIG. 4 is a graph depicting the changes in intensities of peaks in the x-ray diffraction patterns of lithiated MnO_2 neutralized to various pH levels.

FIG. 5 is a graph depicting the cyclic voltammograms of MnO_2 neutralized to various pH levels.

5 FIG. 6 is a graph depicting capacity and lithium content in MnO_2 neutralized to various pH levels.

FIG. 7 is a graph depicting the operating voltage dependence on lithium content in a lithiated MnO_2 .

10 FIG. 8 is a graph depicting the operating voltage and discharge capacity of lithiated MnO_2 having different lithium contents.

FIG. 9 is a graph depicting the operating voltage and discharge capacity of lithiated MnO_2 obtained at pH 11 and an EMD.

Ion exchange of surface protons of manganese oxide with lithium ions can result in formation of the lithiated manganese oxide upon heat treatment.

15 The lithiated manganese oxide is a new MnO_2 phase. Generally, preparation of electrochemically produced manganese dioxide (EMD) involves exposing manganese dioxide to a strong acid, such as sulfuric acid, which is eventually neutralized with a base, such as lithium hydroxide. By washing EMD with lithium hydroxide, a lithium grade MnO_2 is produced which has a low sodium content and can be used in

20 primary lithium cells. EMD is commercially available from, for example, Delta E.M.D. (Pty) Ltd., Nelspruit, South Africa, and Kerr-McGee Chemical Co., Oklahoma City, Oklahoma.

Neutralization of EMD with lithium hydroxide to a pH higher than about 7, preferably to a pH higher than about 9, and more preferably to a pH higher

25 than about 11, can produce a lithiated manganese oxide with desirable electrochemical properties for use in electrochemical cells.

More specifically, LiOH is added to a MnO_2 (e.g., EMD) suspension in water until a saturation level is reached. This typically occurs at pH greater than 7 (e.g., greater than 11). After raising the pH, the MnO_2 is isolated from water and

30 heat treated to a temperature between about 350 and 400°C. The new crystallographic phase of lithiated manganese oxide is produced by this procedure.

The lithiated manganese oxide generated by lithiation to a pH greater

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than 7 leads to an increase in operating voltage of lithium cells containing the material, an increased lithium content of the material, a decrease in the Mn^{4+} content of the material, and a higher reversibility as a recyclable cathode. The lithiated manganese oxide can be identified by cyclic voltammetry and x-ray diffraction.

5 The lithiated manganese oxide can be incorporated into an electrode of a primary storage cell, or battery. A primary storage cell includes a negative electrode in electrical contact with negative lead or contact, a positive electrode in electrical contact with positive lead or contact. The positive electrode includes the lithiated manganese oxide. The negative electrode includes lithium. The electrode
10 material is mixed with a polymeric binding medium to produce a paste which can be applied to a highly porous sintered, felt, or foam substrate. Electrode pieces of the appropriate size can be cut from the substrate.

A separator is located between the electrodes. The separator prevents the positive and negative electrodes from making electrical contact. The separator is
15 a porous polymer film or thin sheet that serves as a spacer and is composed of relatively non-reactive polymers such as, for example, polypropylene, polyethylene, a polyamide (i.e., a nylon), a polysulfone, or polyvinyl chloride (PVC). The separator is porous and prevents contact between the electrodes while allowing the electrolyte to move through the pores. The preferred separator has a thickness
20 between about 10 microns to 200 microns, more preferably between about 20 microns to 50 microns.

The electrodes and the separator are contained within a case. The case can form a coin cell, button cell, prismatic cell, or other standard cell geometry. The case is closed to provide a gas-tight and fluid-tight seal. The case
25 can be made of a metal such as nickel or nickel plated steel, or a plastic material such as PVC, polypropylene, a polysulfone, ABS, or a polyamide.

The case containing the electrodes and separator is filled with an electrolyte. The electrolyte may be any electrolyte known in the art. A preferred electrolyte is a 0.6M solution of lithium trifluoromethylsulfonate (CF_3SO_3Li ; LITFS)
30 in an ethylene carbonate (EC)/propylene carbonate (PC)/dimethoxyethane (DME) mixture. Once filled with electrolyte, the case is sealed. The operating voltage of a lithium battery, or a Li/MnO_2 cell, can be increased by treating the manganese

dioxide with a lithium salt, such as lithium hydroxide, to high pH.

The following examples illustrate the invention.

Example 1

The lithiated manganese oxide was prepared by treating EMD with a
5 lithium salt, such as lithium hydroxide, to high pH. Commercial lithium grade EMD (e.g., less than 500 ppm Na) EMD having an initial of pH 4.4 was used as a starting material. EMD can be prepared according to the method described, for example, in U.S. Pat. No. 5,698,176, incorporated herein by reference.

Water was added to the EMD to form a slurry. The pH level of the
10 EMD was increased by addition of LiOH sequentially until the saturation level was reached to a pH of about 12.7. When the pH stabilized, the mixture was stirred overnight to enable the lithium to fully incorporate into the manganese oxide. The next day, the pH dropped and more LiOH was added to achieve the desired pH. The mixture was stirred for one hour once the pH stabilized. Batches at pH 7, 9
15 and 11 were also prepared. Varying amounts of LiOH were added to adjust the pH. For example, to reach a pH of 9 using 2 kg of the Li grade EMD, approximately 27 g of LiOH was added and to reach a pH of 12, about 100 g of LiOH was added. The lithiated manganese oxide was recovered by filtration and was subsequently heated to about 380°C for about four hours.

20 X-ray diffraction analysis of the heat treated lithiated manganese oxide samples prepared by neutralization to pH 11 and neutralization to pH 12.7 also suggest that the phase composition of the material leads to the different electrochemical properties of the materials. Referring to FIG. 1, the lithiated manganese oxide prepared at pH 11 was composed of a mixture of phases,
25 including β -MnO₂. Referring to FIG. 2, by comparison, the material prepared by neutralization to pH 12.7 contained significantly less of the β -MnO₂ phase. A new second phase with x-ray diffraction peaks at 24 (2-Theta) and 31 (2-Theta) can be observed clearly in FIG. 2. The appearance of the new phase can be attributed, in part, to the increased lithium content of the lithiated manganese oxide.

30 The presence of the new phase can be followed by a detailed x-ray diffraction analysis of the heat treated, e.g., 380°C for about 8 hours, manganese dioxide neutralized to different pH levels. Referring to FIG. 3, the 2-Theta peak at

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24 and the 2-Theta peak at 31 each shift position depending on the pH of processing. Depending on the neutralization pH, the 2-Theta peak at 24 can be found between about 25 and 24, shifting to lower angles as pH increases. The 2-Theta peak at 31 can be found between about 29.6 and 31.5, shifting to higher angles as pH increases. Referring to FIG. 4, the intensity of each of these two peaks also changes as the neutralization pH changes. The intensity of the 2-Theta peak at 24 increases from about 35 to about 40 percent as the pH increases from 7 to 12.7; the intensity of the 2-Theta peak at 31 increase from about 34.8 to about 37 over the same pH range.

10 BET surface area analysis of the lithiated manganese oxide after heat treatment showed that both pore surface and pore volume decrease for the manganese dioxide that is neutralized at the higher pH levels.

The new phase is not observed by x-ray diffraction or cyclic voltammetry when the manganese dioxide is heat treated prior to neutralization with lithium hydroxide. Neutralization can lead to a sediment phase and a colloidal phase of lithiated manganese oxide. For example, when the EMD was neutralized to a pH between about 5 and about 11 by the addition of lithium hydroxide, a sediment and colloidal suspension of particles formed. The colloidal suspension included the lithiated manganese oxide.

20 As the neutralization pH increased, there was a corresponding increase in the lithium content of the lithiated manganese oxide. The lithium content was determined by inductively coupled plasma atomic emission spectroscopy. Referring to FIG. 6, neutralization to a pH of greater than 9 produced a lithiated manganese oxide having a lithium content of greater than 0.5 percent; neutralization to a pH of greater than 11 produced a lithiated manganese oxide having a lithium content of greater than 0.7 percent; and neutralization to a pH of greater than 12.7 produced a lithiated manganese oxide having a lithium content of greater than 1.2 percent.

Example 2

30 Coin cells were prepared, including the lithiated manganese oxide. CR 2430 SS coin cells were prepared by pressing 600 mg of a mixture containing 75% KS6 graphite and 25% PTFE into the bottom of the coin cell, followed by

pressing a cathode mixture (60% MnO_2 , 35% KS6 and 5% PTFE) containing 100 mg of the lithiated manganese oxide on top of the KS6/PTFE layer. The separator (Celgard 2400) was placed on top of the cathode mixture. A Li metal anode was placed on top of the separator and the electrolyte (0.57M LiTFS in DME/EC/PC in
5 a 70/10/20 volume percent ratio) was added to the cell.

The coin cells were discharged at C/10 (i.e., at a rate in which the cell capacity is discharged in a period of 10 hours). Referring to FIG. 7, the modified lithiated manganese oxide prepared to a pH higher than 7, and particularly to a pH higher than 11, can have an increased operating voltage. Cells containing
10 the lithiated manganese oxide that was neutralized to a pH higher than 9, had an operating voltage at C/10 of at least 2.8V. As the neutralization pH increased to above 11, the operating voltage at C/10 was greater than 2.85V. At a neutralization pH of about 12.7, the operating voltage increased to about 2.95V. By raising the neutralization pH from the initially as received pH of 4.4 to 12.7, the operating
15 voltage gain is about -150 mV.

Referring to FIG. 7, the increased operating voltage correlates to the lithium content of the lithiated manganese oxide. Referring to FIGS. 6 and 7, the lithium content of the lithiated manganese oxide increases as the neutralization pH increases. The lithium content of the lithiated manganese oxide can be determined
20 by ICP. The Mn^{4+} content of the lithiated manganese oxide neutralized to a pH greater than 11 (e.g., pH 12.7) was less than 59 percent (e.g., about 57.7 percent) after heat treatment.

Referring to FIG. 8, coin cells were tested at the high C/2 rate. The lithiated manganese oxide with the highest lithium content had the highest load
25 voltage. The increase in load voltage results in a small decrease in capacity of the cell (mAh/g).

Example 3

Flooded cells were used for electrochemical measurements of the lithiated manganese oxides. A flooded cell is a cell containing excess electrolyte in
30 which electrolyte access does not limit the current of the cell. A three electrode flooded cell was used, as described in N. Ilchev, *J. Power Sources* 35:175-181 (1991). The test cathode was 100 mg of a 60/40 MnO_2 /Teflonized Acetylene Black

(TAB-2) mix pressed on a nickel current collector. The counter and reference electrodes were lithium metal. At -10°C, discharge of flooded cells at a C/10 discharge rate also showed an increase in operating voltage when the neutralization pH was increased. Similar results were observed with three other
5 batches of EMD from Delta (Delta E.M.D. (Pty) Ltd., Nelspruit, South Africa) that were neutralized to high pH with LiOH.

Cyclic voltammetry experiments were carried out using the flooded cells at slow scan rates (e.g., about 0.03 mV/min) on the various batches of manganese oxide that were neutralized to various pH levels by the addition of
10 lithium hydroxide. Referring to FIG. 5, the discharge voltage of the maximum discharge current increases as the neutralization pH increases. The increase is most pronounced when the neutralization pH is greater than 11. Without being bound to any theory, the shift in discharge voltage can be attributed to a lower amount of the β -MnO₂ phase in the lithiated manganese oxide mixture.

15 Example 4

2/3A cells were prepared using EMD from Delta (Delta E.M.D. (Pty) Ltd., Nelspruit, South Africa) (control or comparative cell) and the lithiated manganese oxide prepared at pH 11 (pH 11). All other aspects of the control 2/3A cell and pH 11 2/3A cell were the same. The cells were discharged at 0.9A by
20 pulsing 3 seconds on and 27 seconds off at -10°C. Referring to FIG. 9, the operating voltage of the pH 11 2/3A cell was consistently higher than the output voltage of the control or comparative 2/3A cell.

Other embodiments are within the claims. For example, the lithium content of lithiated manganese oxide can also be increased by, in addition to raising
25 the processing pH, modifying the ion-exchange process in ways including: (1) Using vacuum back fill of the processing chamber to increase accessibility of the lithium salt solution to small manganese dioxide pores (e.g., those with a radius of less than 20 Angstroms); (2) Using an acid leach process by exposing the manganese dioxide to H₂SO₄; (3) Using elevated processing temperature (e.g., close
30 to the water boiling point) during neutralization; or (4) Using alcohol as surfactant to improve the wettability of the manganese dioxide surface.

CLAIMS

1. A manganese oxide composition comprising a lithiated manganese oxide having an x-ray diffraction pattern including a 31 degree 2-Theta peak intensity of at least 35 percent and a 24 degree 2-Theta peak intensity of at least 35 percent.
2. The composition of claim 1, wherein the 31 degree 2-Theta peak intensity is at least 36 percent.
3. The composition of claim 1, wherein the 24 degree 2-Theta peak intensity is at least 38 percent.
4. The composition of claim 1, wherein the 31 degree 2-Theta peak is between 31 degrees and 32 degrees.
5. The composition of claim 1, wherein the 24 degree 2-Theta peak is between 24 degrees and 24.8 degrees.
6. The composition of claim 1, wherein the lithiated manganese dioxide includes greater than about 7 percent lithium in MnO_2 .
7. The composition of claim 1, wherein the lithiated manganese oxide includes less than 59 weight percent Mn^{4+} .
8. An electrochemical cell comprising a first electrode including a lithiated manganese dioxide including greater than about 0.7 weight percent lithium in MnO_2 ; and
a second electrode.
9. The cell of claim 8, wherein the second electrode is a lithium electrode.
10. The cell of claim 8, wherein the second electrode is a lithiated carbon electrode.
11. The cell of claim 8, wherein the cell has an operating voltage of greater than 2.9 V.
12. The cell of claim 8, wherein the lithiated manganese dioxide has an x-ray diffraction pattern including a 31 degree 2-Theta peak intensity of at least 35 percent and a 24 degree 2-Theta peak intensity of at least 35 percent.
13. The cell of claim 8, wherein the 31 degree 2-Theta peak intensity is at least 36 percent.

14. The cell of claim 8, wherein the 24 degree 2-Theta peak intensity is at least 38 percent.
15. The cell of claim 8, wherein the 31 degree 2-Theta peak is between 31 degrees and 32 degrees.
- 5 16. The cell of claim 8, wherein the 24 degree 2-Theta peak is between 24 degrees and 24.8 degrees.
17. A method of manufacturing an electrochemical cell comprising:
preparing an electrode including a lithiated manganese oxide having
an x-ray diffraction pattern including a 31 degree 2-Theta peak intensity of at least
10 35 percent and a 24 degree 2-Theta peak intensity of at least 35 percent; and
forming a cell including the electrode and a lithium electrode.
18. The method of claim 17, wherein preparing the electrode includes:
providing the lithiated manganese oxide.
19. The method of claim 18, wherein providing the lithiated manganese
15 oxide includes:
placing a manganese oxide in a liquid to provide a suspension;
adding a lithium salt to the suspension to provide a suspension at a
pH greater than about 7;
removing the liquid from the suspension to provide a solid; and
20 heating the solid to provide the lithiated manganese oxide.
20. The method of claim 19, wherein the lithium salt is added to the
suspension to provide a suspension at a pH greater than about 11.
21. The method of claim 17, wherein the 31 degree 2-Theta peak
intensity is at least 36 percent.
- 25 22. The method of claim 17, wherein the 24 degree 2-Theta peak
intensity is at least 38 percent.
23. The method of claim 17, wherein the 31 degree 2-Theta peak is
between 31 degrees and 32 degrees.
24. The method of claim 17, wherein the 24 degree 2-Theta peak is
30 between 24 degrees and 24.8 degrees.
25. The method of claim 17, wherein the lithiated manganese dioxide
includes greater than about 0.7 percent lithium in MnO_2 .

26. The method of claim 17, wherein the cell has an operating voltage of greater than 2.9V.
27. A method of preparing a lithiated manganese dioxide comprising:
adding a lithium salt to a suspension of manganese oxide in a liquid;
removing the liquid from the suspension to provide a solid; and
heating the solid to provide a lithiated manganese dioxide having an
x-ray diffraction pattern including a 31 degree 2-Theta peak intensity of at least 35
percent and a 24 degree 2-Theta peak intensity of at least 35 percent.
28. The method of claim 27, wherein the manganese oxide includes an
electrochemically produced manganese dioxide.
29. The method of claim 27, wherein the lithium salt includes lithium
hydroxide.
30. The method of claim 27, wherein adding a lithium salt includes
adding a solution including lithium hydroxide to the suspension.
31. The method of claim 27, wherein the liquid includes water.
32. The method of claim 27, wherein heating includes raising the
temperature of the solid to between about 350°C and 400°C.
33. The method of claim 27, wherein the lithiated manganese dioxide
includes greater than about 0.7 weight percent lithium in MnO_2 .
34. The method of claim 27, wherein the lithiated manganese dioxide
includes less than 59 weight percent Mn^{4+} .
35. The method of claim 27, wherein the lithiated manganese dioxide has
an operating voltage of greater than 2.9V.
36. A method of preparing a lithiated manganese oxide comprising:
adding a lithium salt to a suspension of a manganese oxide in a liquid
to provide a suspension at a pH greater than about 11;
removing the liquid from the suspension to provide a solid; and
heating the solid to provide the lithiated manganese oxide.
37. The method of claim 36, wherein the lithiated manganese dioxide
has an x-ray diffraction pattern including a 31 degree 2-Theta peak intensity of at
least 35 percent and a 24 degree 2-Theta peak intensity of at least 35 percent.

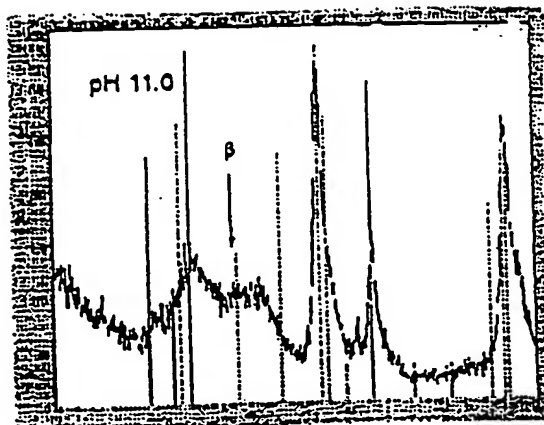


FIG. 1

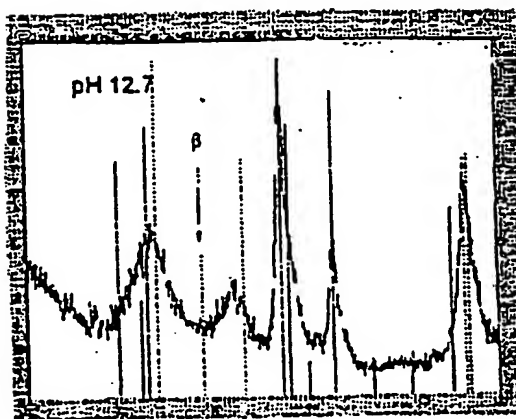


FIG. 2

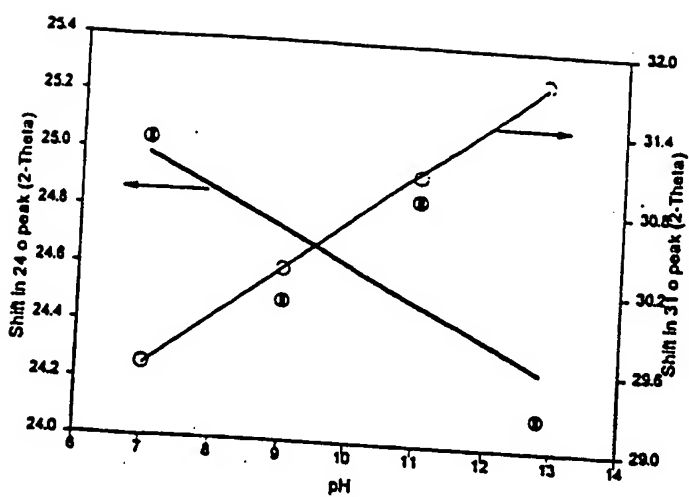


FIG. 3

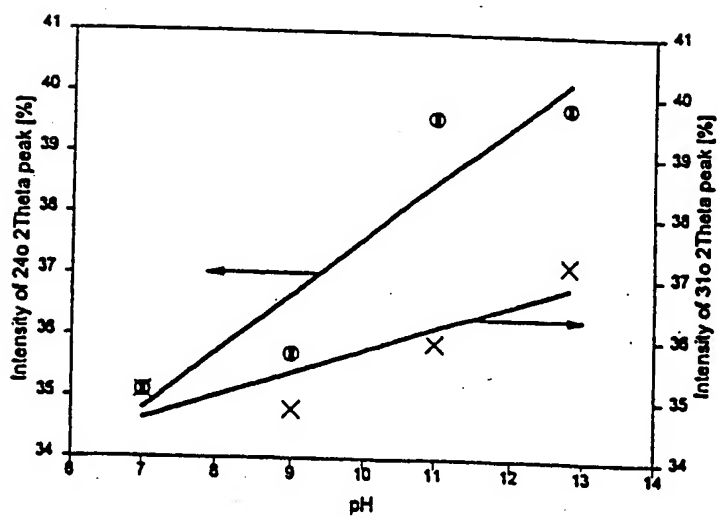


FIG. 4

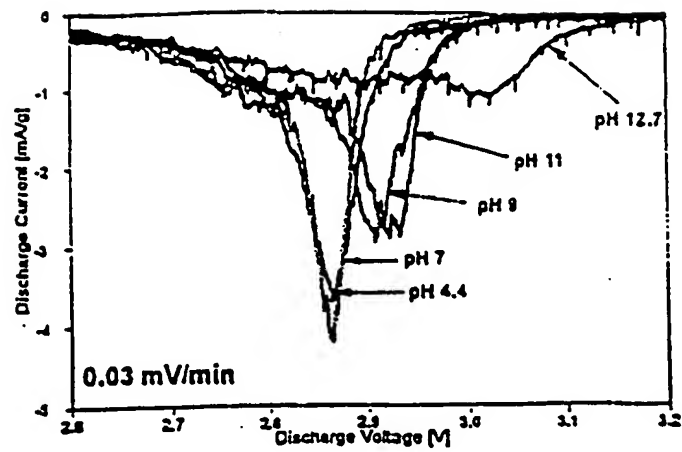


FIG. 5

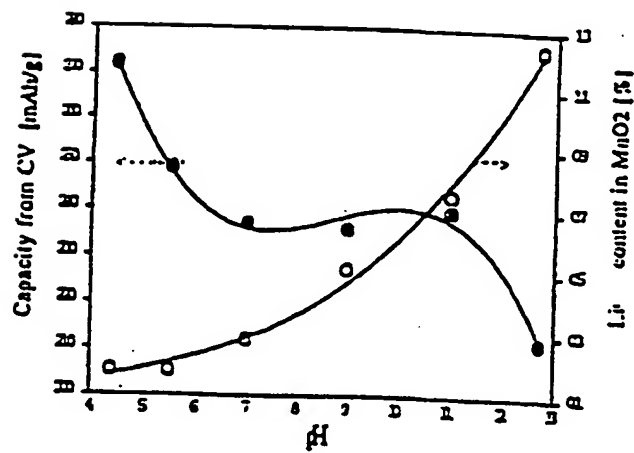


FIG. 6

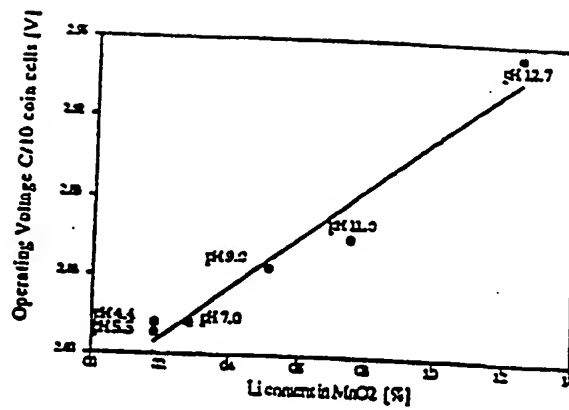


FIG. 7

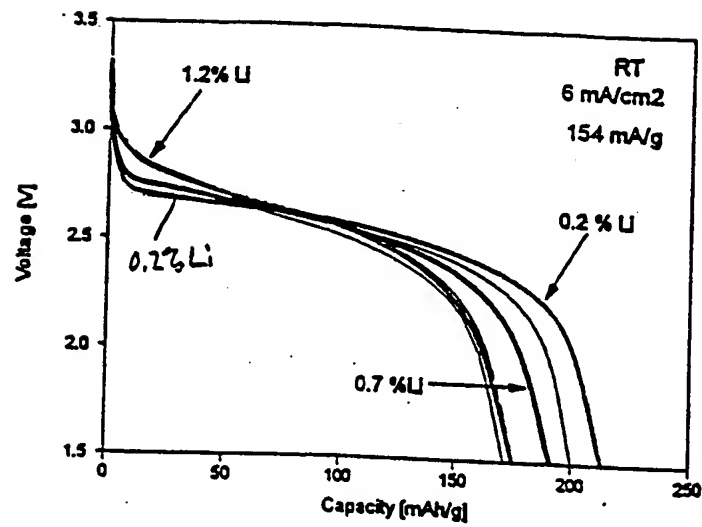


FIG. 8

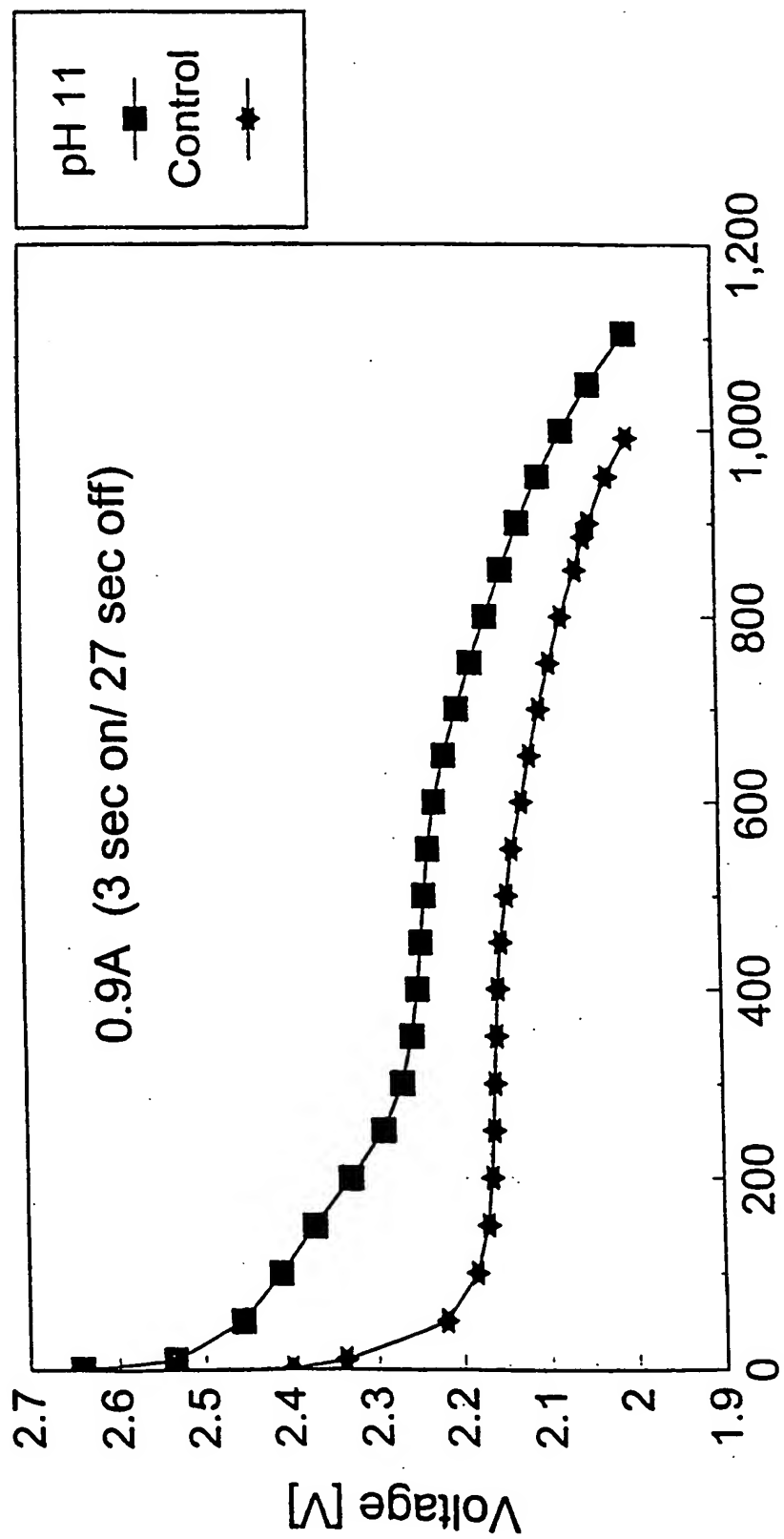


FIG. 9

INTERNATIONAL SEARCH REPORT

Int. .onal Application No

PCT/US 99/10173

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 H01M4/50 C01G45/02 H01M6/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01M C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 014, no. 457 (E-0986), 2 October 1990 (1990-10-02) & JP 02 183963 A (SANYO ELECTRIC CO LTD), 18 July 1990 (1990-07-18)	1-7, 17-26
Y	abstract	8-16, 27-36
X	--- PATENT ABSTRACTS OF JAPAN vol. 013, no. 564 (E-860), 14 December 1989 (1989-12-14) & JP 01 235158 A (SANYO ELECTRIC CO LTD), 20 September 1989 (1989-09-20)	1-7, 17-26
Y	abstract	8-16, 27-36
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☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PATENT ABSTRACTS OF JAPAN vol. 013, no. 562 (C-665), 13 December 1989 (1989-12-13) & JP 01 234329 A (MITSUI MINING & SMELTING CO LTD), 19 September 1989 (1989-09-19) abstract ---	8-36
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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(51) International Patent Classification ⁶ : H01M 4/50, C01G 45/02, H01M 6/14	A1	(11) International Publication Number: WO 99/59215 (43) International Publication Date: 18 November 1999 (18.11.99)
<p>(21) International Application Number: PCT/US99/10173</p> <p>(22) International Filing Date: 10 May 1999 (10.05.99)</p> <p>(30) Priority Data: 09/075,586 11 May 1998 (11.05.98) US</p> <p>(71) Applicant: DURACELL INC. [US/US]; Berkshire Corporate Park, Bethel, CT 06801 (US).</p> <p>(72) Inventors: MOSES, Peter, R.; 61 Kendall Pond Road, Windham, NH 03087 (US). BOWDEN, William, L.; 28 Cathedral Circle, Nashua, NH 03063 (US). ILTCHEV, Nikolay; 1 Old Colony Road, Norfolk, MA 02156 (US). BRANDT, Klaus; 50 Summit Road, Wellesley, MA 02181 (US).</p> <p>(74) Agents: HANDELMAN, Joseph, H.; Ladas & Parry, 26 West 61st Street, New York, NY 10023 (US) et al.</p>	<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>	
<p>(54) Title: LITHIATED MANGANESE OXIDE</p> <p>(57) Abstract</p> <p>A lithiated manganese oxide for use in primary lithium cells is described. The lithiated manganese oxide can be prepared by exposure to a lithium source under conditions that result in the formation of a modified manganese oxide phase. When the modified phase is used in a primary lithium cell, the operating voltage of an electrochemical cell containing the lithiated manganese oxide increases relative to the operating voltage of a cell containing a manganese dioxide that is not exposed to the lithium source.</p>		

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LITHIATED MANGANESE OXIDE

This invention relates to lithium electrochemical cells.

A battery includes one or more galvanic cells (i.e., cells that produce a direct current of electricity) in a finished package. Cells of this type generally contain two electrodes separated by a liquid capable of transporting ions, called an electrolyte. Typical electrolytes include liquid organic electrolyte or a polymeric electrolyte. The cell produces electricity from chemical reactions through oxidation at one electrode, commonly referred to as the negative electrode, and reduction at the other electrode, commonly referred to as the positive electrode. Completion of an electronically conducting circuit including the negative and positive electrodes allows ion transport across the cell and discharges the battery. A primary battery is meant to be discharged to exhaustion once, and then discarded. A rechargeable battery can be charged and discharged multiple times.

An example of a primary battery is a primary lithium cell. A lithium electrochemical cell is a galvanic cell using lithium, a lithium alloy or other lithium containing material as one electrode in the cell. The other electrode of the cell can include, for example; a metal oxide, such as a manganese dioxide (e.g., $\gamma,\beta\text{-MnO}_2$). The metal oxide used in the electrode can be processed prior to use in a lithium battery. Generally, manganese dioxide can be prepared by chemical methods or electrochemical methods. The resulting materials are known as chemically produced manganese dioxide (CMD) and electrochemically produced (e.g., electrolytic) manganese dioxide (EMD), respectively. A rechargeable battery, such as a lithium ion battery, can include a lithiated carbon electrode.

Manganese dioxide-based lithium cells are described, for example, in Ikeda, et al. "Manganese Dioxide as Cathodes for Lithium Batteries," in Manganese Dioxide Symposium, Vol. 1, The Electrochemical Society, Cleveland Section, 1975, p. 384-401, incorporated herein by reference.

The invention relates to a lithiated manganese oxide for use in electrochemical cells. The lithiated manganese oxide can be prepared by exposure to a lithium source under conditions that results in the formation of a modified manganese oxide phase. When the modified phase is used in a primary lithium cell, the operating voltage of an electrochemical cell containing the lithiated manganese

oxide increases relative to the operating voltage of a cell containing a manganese dioxide that is not exposed to the lithium source.

In one aspect, the invention features a manganese oxide composition that includes a lithiated manganese oxide. The lithiated manganese oxide can have
5 an x-ray diffraction pattern including a 31 degree 2-Theta peak intensity of at least 35 percent and a 24 degree 2-Theta peak intensity of at least 35 percent.

In certain embodiments, the 31 degree 2-Theta peak intensity can be at least 36 percent. In other embodiments, the 24 degree 2-Theta peak intensity can be at least 38 percent. The 31 degree 2-Theta peak can be between 31 degrees and
10 32 degrees. The 24 degree 2-Theta peak can be between 24 degrees and 24.8 degrees.

The lithiated manganese oxide can have a discharge voltage of greater than 2.9V when tested in a CR 2430 coin cell (e.g., a primary lithium cell) at 1 mA/cm² continuous discharge at room temperature. It also can include greater than
15 about 0.7 weight percent (e.g., greater than 1.0 weight percent) lithium in MnO₂ and less than 59 weight percent Mn⁴⁺.

In another aspect, the invention features a method of preparing a lithiated manganese oxide.

In the method, a manganese oxide is placed in a liquid to provide a
20 suspension. The manganese oxide can be an electrochemically produced manganese dioxide (EMD). The liquid can be water.

A lithium salt is added to the suspension. The lithium salt can be lithium hydroxide. The pH of the suspension can be increased so that it is basic, such as to a pH greater than about 7, preferably greater than about 9, and more
25 preferably greater than about 11. For example, the pH of the suspension can be increased by adding a solution including lithium hydroxide to the suspension.

After adding the lithium salt, the liquid is removed to provide a solid. The liquid can be removed by filtering the suspension, centrifuging the suspension, or evaporating the liquid, or combinations thereof. The solid can be a sediment, a
30 particle or group of particles collected from a colloid, or a combination thereof.

The solid is heated to provide the lithiated manganese oxide. Heating can include raising the temperature of the solid to between about 350°C and 400°C.

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In another aspect, the invention features an electrochemical cell including a first electrode and a second electrode. The second electrode can be a lithium electrode or a lithiated carbon electrode. The electrode can include a lithiated manganese oxide. The cell can have a discharge voltage of greater than
5 2.9V.

In another aspect, the invention features a method of manufacturing a lithium cell. The method includes preparing an electrode including a lithiated manganese oxide. The lithiated manganese oxide of the electrode can be prepared by placing a manganese oxide in a liquid to provide a suspension, adding a lithium
10 salt to the suspension to provide a suspension at a pH greater than about 11, removing the liquid from the suspension to provide a solid, and heating the solid to provide the lithiated manganese oxide.

The lithiated manganese oxide can have the following advantages. For example, the battery load voltage suppression can be improved by increasing the
15 lithium content of the MnO_2 . At the beginning of a heavy load low temperature discharge curve of lithium grade MnO_2 , the battery load voltage can be suppressed. Accordingly, the uses of the battery can be limited by the performance of the material, e.g., the suppressed load voltage does not meet the requirements for photographic camera applications. The lithium content of the manganese oxide can
20 be increased by carrying out the neutralization step to higher pH levels (e.g., greater than about 9). In the subsequent processing and drying of EMD to make it suitable for lithium batteries, the additional lithium can react with MnO_2 to form the lithiated manganese oxide. The lithiated manganese oxide can lead to an increase of the load voltage, especially at heavy discharge rates and at low temperatures.

25 Other features and advantages of the invention will be apparent from the description of the preferred embodiments and from the claims.

FIG. 1 is a graph depicting an x-ray diffraction pattern of a lithiated MnO_2 .

FIG. 2 is a graph depicting an x-ray diffraction pattern of a lithiated
30 MnO_2 .

FIG. 3 is a graph depicting the shifts in peak locations in the x-ray diffraction patterns of lithiated MnO_2 neutralized to various pH levels.

FIG. 4 is a graph depicting the changes in intensities of peaks in the x-ray diffraction patterns of lithiated MnO_2 neutralized to various pH levels.

FIG. 5 is a graph depicting the cyclic voltammograms of MnO_2 neutralized to various pH levels.

5 FIG. 6 is a graph depicting capacity and lithium content in MnO_2 neutralized to various pH levels.

FIG. 7 is a graph depicting the operating voltage dependance on lithium content in a lithiated MnO_2 .

10 FIG. 8 is a graph depicting the operating voltage and discharge capacity of lithiated MnO_2 having different lithium contents.

FIG. 9 is a graph depicting the operating voltage and discharge capacity of lithiated MnO_2 obtained at pH 11 and an EMD.

Ion exchange of surface protons of manganese oxide with lithium ions can result in formation of the lithiated manganese oxide upon heat treatment.

15 The lithiated manganese oxide is a new MnO_2 phase. Generally, preparation of electrochemically produced manganese dioxide (EMD) involves exposing manganese dioxide to a strong acid, such as sulfuric acid, which is eventually neutralized with a base, such as lithium hydroxide. By washing EMD with lithium hydroxide, a lithium grade MnO_2 is produced which has a low sodium content and can be used in

20 primary lithium cells. EMD is commercially available from, for example, Delta E.M.D. (Pty) Ltd., Nelspruit, South Africa, and Kerr-McGee Chemical Co., Oklahoma City, Oklahoma.

Neutralization of EMD with lithium hydroxide to a pH higher than about 7, preferably to a pH higher than about 9, and more preferably to a pH higher

25 than about 11, can produce a lithiated manganese oxide with desirable electrochemical properties for use in electrochemical cells.

More specifically, LiOH is added to a MnO_2 (e.g., EMD) suspension in water until a saturation level is reached. This typically occurs at pH greater than 7 (e.g., greater than 11). After raising the pH, the MnO_2 is isolated from water and

30 heat treated to a temperature between about 350 and 400°C. The new crystallographic phase of lithiated manganese oxide is produced by this procedure.

The lithiated manganese oxide generated by lithiation to a pH greater

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than 7 leads to an increase in operating voltage of lithium cells containing the material, an increased lithium content of the material, a decrease in the Mn^{4+} content of the material, and a higher reversibility as a recyclable cathode. The lithiated manganese oxide can be identified by cyclic voltammetry and x-ray diffraction.

5 The lithiated manganese oxide can be incorporated into an electrode of a primary storage cell, or battery. A primary storage cell includes a negative electrode in electrical contact with negative lead or contact, a positive electrode in electrical contact with positive lead or contact. The positive electrode includes the lithiated manganese oxide. The negative electrode includes lithium. The electrode
10 material is mixed with a polymeric binding medium to produce a paste which can be applied to a highly porous sintered, felt, or foam substrate. Electrode pieces of the appropriate size can be cut from the substrate.

A separator is located between the electrodes. The separator prevents the positive and negative electrodes from making electrical contact. The separator is
15 a porous polymer film or thin sheet that serves as a spacer and is composed of relatively non-reactive polymers such as, for example, polypropylene, polyethylene, a polyamide (i.e., a nylon), a polysulfone, or polyvinyl chloride (PVC). The separator is porous and prevents contact between the electrodes while allowing the electrolyte to move through the pores. The preferred separator has a thickness
20 between about 10 microns to 200 microns, more preferably between about 20 microns to 50 microns.

The electrodes and the separator are contained within a case. The case can form a coin cell, button cell, prismatic cell, or other standard cell geometry. The case is closed to provide a gas-tight and fluid-tight seal. The case
25 can be made of a metal such as nickel or nickel plated steel, or a plastic material such as PVC, polypropylene, a polysulfone, ABS, or a polyamide.

The case containing the electrodes and separator is filled with an electrolyte. The electrolyte may be any electrolyte known in the art. A preferred electrolyte is a 0.6M solution of lithium trifluoromethylsulfonate (CF_3SO_3Li ; LITFS)
30 in an ethylene carbonate (EC)/propylene carbonate (PC)/dimethoxyethane (DME) mixture. Once filled with electrolyte, the case is sealed. The operating voltage of a lithium battery, or a Li/MnO_2 cell, can be increased by treating the manganese

dioxide with a lithium salt, such as lithium hydroxide, to high pH.

The following examples illustrate the invention.

Example 1

The lithiated manganese oxide was prepared by treating EMD with a
5 lithium salt, such as lithium hydroxide, to high pH. Commercial lithium grade EMD (e.g., less than 500 ppm Na) EMD having an initial of pH 4.4 was used as a starting material. EMD can be prepared according to the method described, for example, in U.S. Pat. No. 5,698,176, incorporated herein by reference.

Water was added to the EMD to form a slurry. The pH level of the
10 EMD was increased by addition of LiOH sequentially until the saturation level was reached to a pH of about 12.7. When the pH stabilized, the mixture was stirred overnight to enable the lithium to fully incorporate into the manganese oxide. The next day, the pH dropped and more LiOH was added to achieve the desired pH. The mixture was stirred for one hour once the pH stabilized. Batches at pH 7, 9
15 and 11 were also prepared. Varying amounts of LiOH were added to adjust the pH. For example, to reach a pH of 9 using 2 kg of the Li grade EMD, approximately 27 g of LiOH was added and to reach a pH of 12, about 100 g of LiOH was added. The lithiated manganese oxide was recovered by filtration and was subsequently heated to about 380°C for about four hours.

20 X-ray diffraction analysis of the heat treated lithiated manganese oxide samples prepared by neutralization to pH 11 and neutralization to pH 12.7 also suggest that the phase composition of the material leads to the different electrochemical properties of the materials. Referring to FIG. 1, the lithiated manganese oxide prepared at pH 11 was composed of a mixture of phases,
25 including β -MnO₂. Referring to FIG. 2, by comparison, the material prepared by neutralization to pH 12.7 contained significantly less of the β -MnO₂ phase. A new second phase with x-ray diffraction peaks at 24 (2-Theta) and 31 (2-Theta) can be observed clearly in FIG. 2. The appearance of the new phase can be attributed, in part, to the increased lithium content of the lithiated manganese oxide.

30 The presence of the new phase can be followed by a detailed x-ray diffraction analysis of the heat treated, e.g., 380°C for about 8 hours, manganese dioxide neutralized to different pH levels. Referring to FIG. 3, the 2-Theta peak at

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24 and the 2-Theta peak at 31 each shift position depending on the pH of processing. Depending on the neutralization pH, the 2-Theta peak at 24 can be found between about 25 and 24, shifting to lower angles as pH increases. The 2-Theta peak at 31 can be found between about 29.6 and 31.5, shifting to higher
5 angles as pH increases. Referring to FIG. 4, the intensity of each of these two peaks also changes as the neutralization pH changes. The intensity of the 2-Theta peak at 24 increases from about 35 to about 40 percent as the pH increases from 7 to 12.7; the intensity of the 2-Theta peak at 31 increase from about 34.8 to about 37 over the same pH range.

10 BET surface area analysis of the lithiated manganese oxide after heat treatment showed that both pore surface and pore volume decrease for the manganese dioxide that is neutralized at the higher pH levels.

The new phase is not observed by x-ray diffraction or cyclic
15 voltammetry when the manganese dioxide is heat treated prior to neutralization with lithium hydroxide. Neutralization can lead to a sediment phase and a colloidal phase of lithiated manganese oxide. For example, when the EMD was neutralized to a pH between about 5 and about 11 by the addition of lithium hydroxide, a sediment and colloidal suspension of particles formed. The colloidal suspension included the lithiated manganese oxide.

20 As the neutralization pH increased, there was a corresponding increase in the lithium content of the lithiated manganese oxide. The lithium content was determined by inductively coupled plasma atomic emission spectroscopy. Referring to FIG. 6, neutralization to a pH of greater than 9 produced a lithiated manganese oxide having a lithium content of greater than 0.5 percent;
25 neutralization to a pH of greater than 11 produced a lithiated manganese oxide having a lithium content of greater than 0.7 percent; and neutralization to a pH of greater than 12.7 produced a lithiated manganese oxide having a lithium content of greater than 1.2 percent.

Example 2

30 Coin cells were prepared, including the lithiated manganese oxide. CR 2430 SS coin cells were prepared by pressing 600 mg of a mixture containing 75% KS6 graphite and 25% PTFE into the bottom of the coin cell, followed by

pressing a cathode mixture (60% MnO_2 , 35% KS6 and 5% PTFE) containing 100 mg of the lithiated manganese oxide on top of the KS6/PTFE layer. The separator (Celgard 2400) was placed on top of the cathode mixture. A Li metal anode was placed on top of the separator and the electrolyte (0.57M LiTFS in DME/EC/PC in a 70/10/20 volume percent ratio) was added to the cell.

The coin cells were discharged at C/10 (i.e., at a rate in which the cell capacity is discharged in a period of 10 hours). Referring to FIG. 7, the modified lithiated manganese oxide prepared to a pH higher than 7, and particularly to a pH higher than 11, can have an increased operating voltage. Cells containing the lithiated manganese oxide that was neutralized to a pH higher than 9, had an operating voltage at C/10 of at least 2.8V. As the neutralization pH increased to above 11, the operating voltage at C/10 was greater than 2.85V. At a neutralization pH of about 12.7, the operating voltage increased to about 2.95V. By raising the neutralization pH from the initially as received pH of 4.4 to 12.7, the operating voltage gain is about -150 mV.

Referring to FIG. 7, the increased operating voltage correlates to the lithium content of the lithiated manganese oxide. Referring to FIGS. 6 and 7, the lithium content of the lithiated manganese oxide increases as the neutralization pH increases. The lithium content of the lithiated manganese oxide can be determined by ICP. The Mn^{4+} content of the lithiated manganese oxide neutralized to a pH greater than 11 (e.g., pH 12.7) was less than 59 percent (e.g., about 57.7 percent) after heat treatment.

Referring to FIG. 8, coin cells were tested at the high C/2 rate. The lithiated manganese oxide with the highest lithium content had the highest load voltage. The increase in load voltage results in a small decrease in capacity of the cell (mAh/g).

Example 3

Flooded cells were used for electrochemical measurements of the lithiated manganese oxides. A flooded cell is a cell containing excess electrolyte in which electrolyte access does not limit the current of the cell. A three electrode flooded cell was used, as described in N. Ilchev, *J. Power Sources* 35:175-181 (1991). The test cathode was 100 mg of a 60/40 MnO_2 /Teflonized Acetylene Black

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(TAB-2) mix pressed on a nickel current collector. The counter and reference electrodes were lithium metal. At -10°C, discharge of flooded cells at a C/10 discharge rate also showed an increase in operating voltage when the neutralization pH was increased. Similar results were observed with three other
5 batches of EMD from Delta (Delta E.M.D. (Pty) Ltd., Nelspruit, South Africa) that were neutralized to high pH with LiOH.

Cyclic voltammetry experiments were carried out using the flooded cells at slow scan rates (e.g., about 0.03 mV/min) on the various batches of manganese oxide that were neutralized to various pH levels by the addition of
10 lithium hydroxide. Referring to FIG. 5, the discharge voltage of the maximum discharge current increases as the neutralization pH increases. The increase is most pronounced when the neutralization pH is greater than 11. Without being bound to any theory, the shift in discharge voltage can be attributed to a lower amount of the β -MnO₂ phase in the lithiated manganese oxide mixture.

15

Example 4

2/3A cells were prepared using EMD from Delta (Delta E.M.D. (Pty) Ltd., Nelspruit, South Africa) (control or comparative cell) and the lithiated manganese oxide prepared at pH 11 (pH 11). All other aspects of the control 2/3A cell and pH 11 2/3A cell were the same. The cells were discharged at 0.9A by
20 pulsing 3 seconds on and 27 seconds off at -10°C. Referring to FIG. 9, the operating voltage of the pH 11 2/3A cell was consistently higher than the output voltage of the control or comparative 2/3A cell.

Other embodiments are within the claims. For example, the lithium content of lithiated manganese oxide can also be increased by, in addition to raising
25 the processing pH, modifying the ion-exchange process in ways including: (1) Using vacuum back fill of the processing chamber to increase accessibility of the lithium salt solution to small manganese dioxide pores (e.g., those with a radius of less than 20 Angstroms); (2) Using an acid leach process by exposing the manganese dioxide to H₂SO₄; (3) Using elevated processing temperature (e.g., close
30 to the water boiling point) during neutralization; or (4) Using alcohol as surfactant to improve the wettability of the manganese dioxide surface.

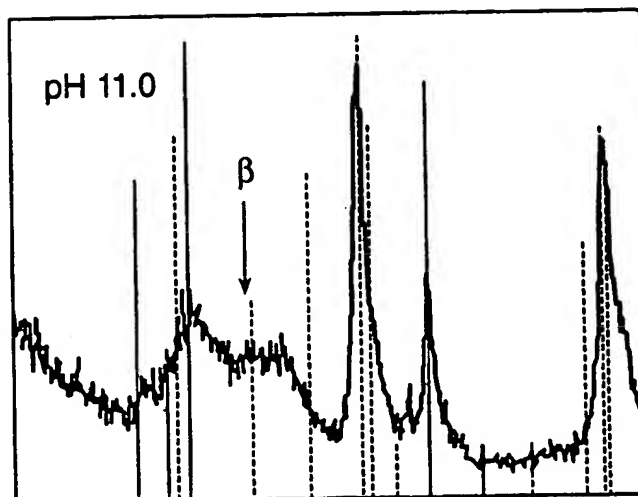
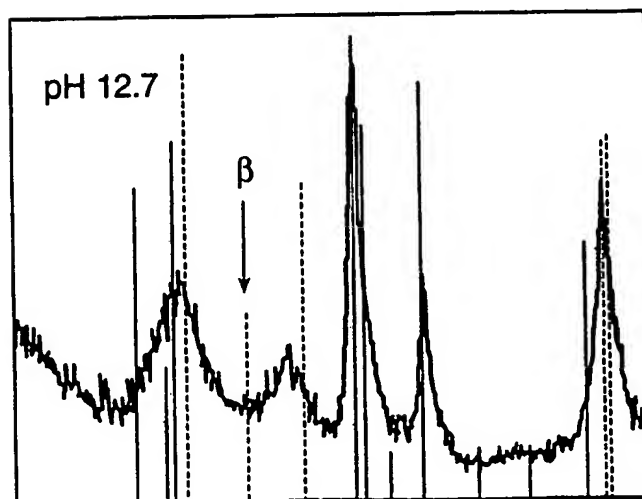
CLAIMS

1. A manganese oxide composition comprising a lithiated manganese oxide having an x-ray diffraction pattern including a 31 degree 2-Theta peak intensity of at least 35 percent and a 24 degree 2-Theta peak intensity of at least 35 percent.
2. The composition of claim 1, wherein the 31 degree 2-Theta peak intensity is at least 36 percent.
3. The composition of claim 1, wherein the 24 degree 2-Theta peak intensity is at least 38 percent.
4. The composition of claim 1, wherein the 31 degree 2-Theta peak is between 31 degrees and 32 degrees.
5. The composition of claim 1, wherein the 24 degree 2-Theta peak is between 24 degrees and 24.8 degrees.
6. The composition of claim 1, wherein the lithiated manganese dioxide includes greater than about 7 percent lithium in MnO_2 .
7. The composition of claim 1, wherein the lithiated manganese oxide includes less than 59 weight percent Mn^{4+} .
8. An electrochemical cell comprising a first electrode including a lithiated manganese dioxide including greater than about 0.7 weight percent lithium in MnO_2 ; and
a second electrode.
9. The cell of claim 8, wherein the second electrode is a lithium electrode.
10. The cell of claim 8, wherein the second electrode is a lithiated carbon electrode.
11. The cell of claim 8, wherein the cell has an operating voltage of greater than 2.9 V.
12. The cell of claim 8, wherein the lithiated manganese dioxide has an x-ray diffraction pattern including a 31 degree 2-Theta peak intensity of at least 35 percent and a 24 degree 2-Theta peak intensity of at least 35 percent.
13. The cell of claim 8, wherein the 31 degree 2-Theta peak intensity is at least 36 percent.

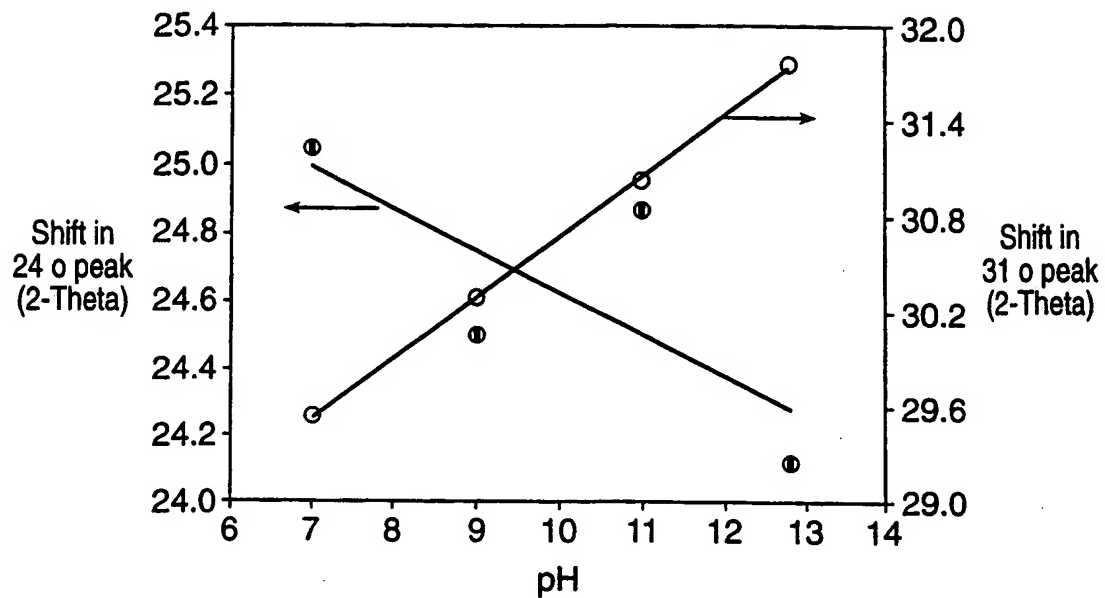
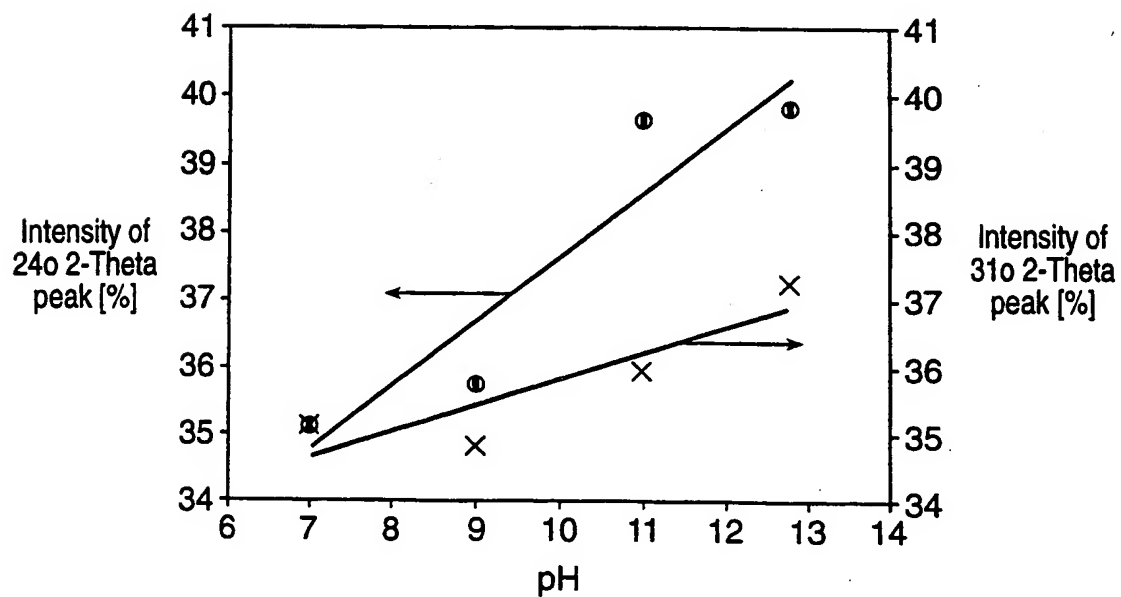
14. The cell of claim 8, wherein the 24 degree 2-Theta peak intensity is at least 38 percent.
15. The cell of claim 8, wherein the 31 degree 2-Theta peak is between 31 degrees and 32 degrees.
- 5 16. The cell of claim 8, wherein the 24 degree 2-Theta peak is between 24 degrees and 24.8 degrees.
17. A method of manufacturing an electrochemical cell comprising:
preparing an electrode including a lithiated manganese oxide having an x-ray diffraction pattern including a 31 degree 2-Theta peak intensity of at least
10 35 percent and a 24 degree 2-Theta peak intensity of at least 35 percent; and
forming a cell including the electrode and a lithium electrode.
18. The method of claim 17, wherein preparing the electrode includes:
providing the lithiated manganese oxide.
19. The method of claim 18, wherein providing the lithiated manganese
15 oxide includes:
placing a manganese oxide in a liquid to provide a suspension;
adding a lithium salt to the suspension to provide a suspension at a
pH greater than about 7;
removing the liquid from the suspension to provide a solid; and
20 heating the solid to provide the lithiated manganese oxide.
20. The method of claim 19, wherein the lithium salt is added to the suspension to provide a suspension at a pH greater than about 11.
21. The method of claim 17, wherein the 31 degree 2-Theta peak intensity is at least 36 percent.
- 25 22. The method of claim 17, wherein the 24 degree 2-Theta peak intensity is at least 38 percent.
23. The method of claim 17, wherein the 31 degree 2-Theta peak is between 31 degrees and 32 degrees.
24. The method of claim 17, wherein the 24 degree 2-Theta peak is
30 between 24 degrees and 24.8 degrees.
25. The method of claim 17, wherein the lithiated manganese dioxide includes greater than about 0.7 percent lithium in MnO_2 .

26. The method of claim 17, wherein the cell has an operating voltage of greater than 2.9V.
27. A method of preparing a lithiated manganese dioxide comprising:
adding a lithium salt to a suspension of manganese oxide in a liquid;
5 removing the liquid from the suspension to provide a solid; and
heating the solid to provide a lithiated manganese dioxide having an x-ray diffraction pattern including a 31 degree 2-Theta peak intensity of at least 35 percent and a 24 degree 2-Theta peak intensity of at least 35 percent.
28. The method of claim 27, wherein the manganese oxide includes an
10 electrochemically produced manganese dioxide.
29. The method of claim 27, wherein the lithium salt includes lithium hydroxide.
30. The method of claim 27, wherein adding a lithium salt includes adding a solution including lithium hydroxide to the suspension.
- 15 31. The method of claim 27, wherein the liquid includes water.
32. The method of claim 27, wherein heating includes raising the temperature of the solid to between about 350°C and 400°C.
33. The method of claim 27, wherein the lithiated manganese dioxide includes greater than about 0.7 weight percent lithium in MnO_2 .
- 20 34. The method of claim 27, wherein the lithiated manganese dioxide includes less than 59 weight percent Mn^{4+} .
35. The method of claim 27, wherein the lithiated manganese dioxide has an operating voltage of greater than 2.9V.
36. A method of preparing a lithiated manganese oxide comprising:
25 adding a lithium salt to a suspension of a manganese oxide in a liquid to provide a suspension at a pH greater than about 11;
removing the liquid from the suspension to provide a solid; and
heating the solid to provide the lithiated manganese oxide.
37. The method of claim 36, wherein the lithiated manganese dioxide
30 has an x-ray diffraction pattern including a 31 degree 2-Theta peak intensity of at least 35 percent and a 24 degree 2-Theta peak intensity of at least 35 percent.

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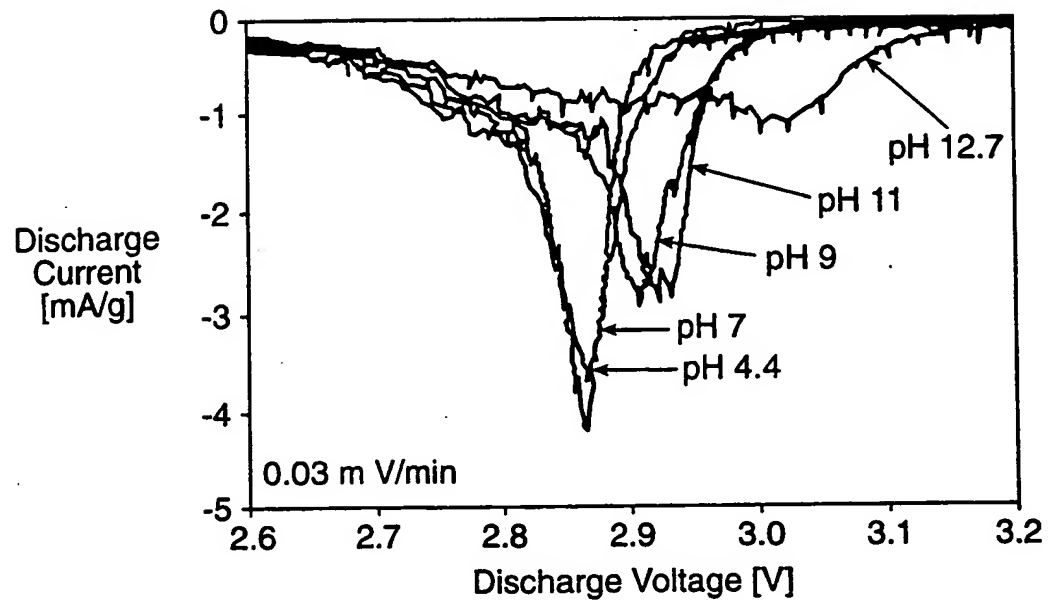
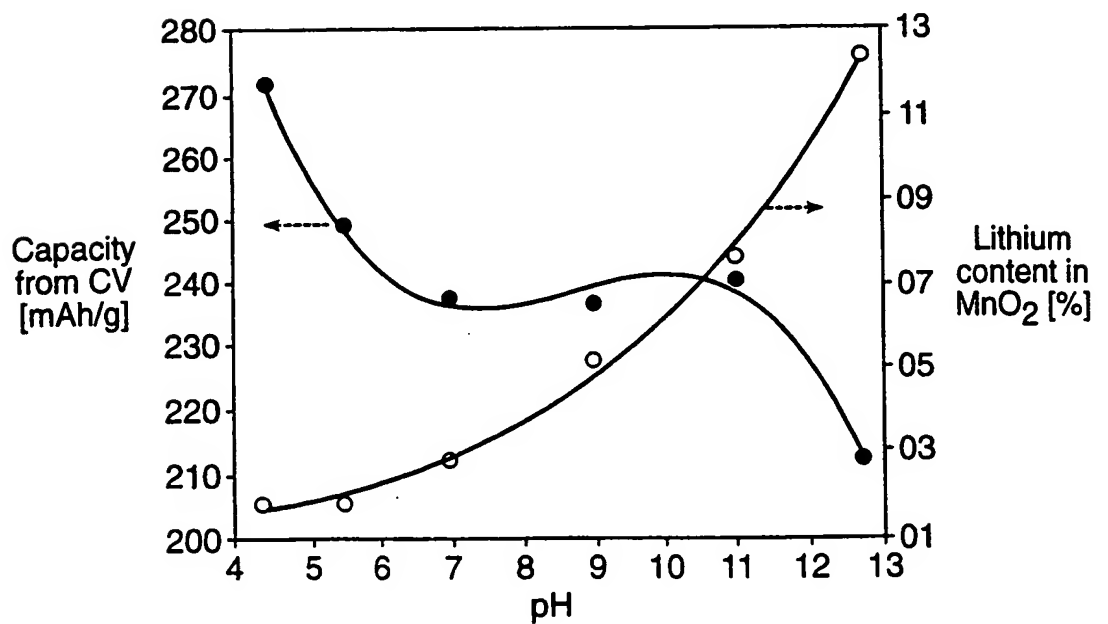
FIG. 1**FIG. 2**

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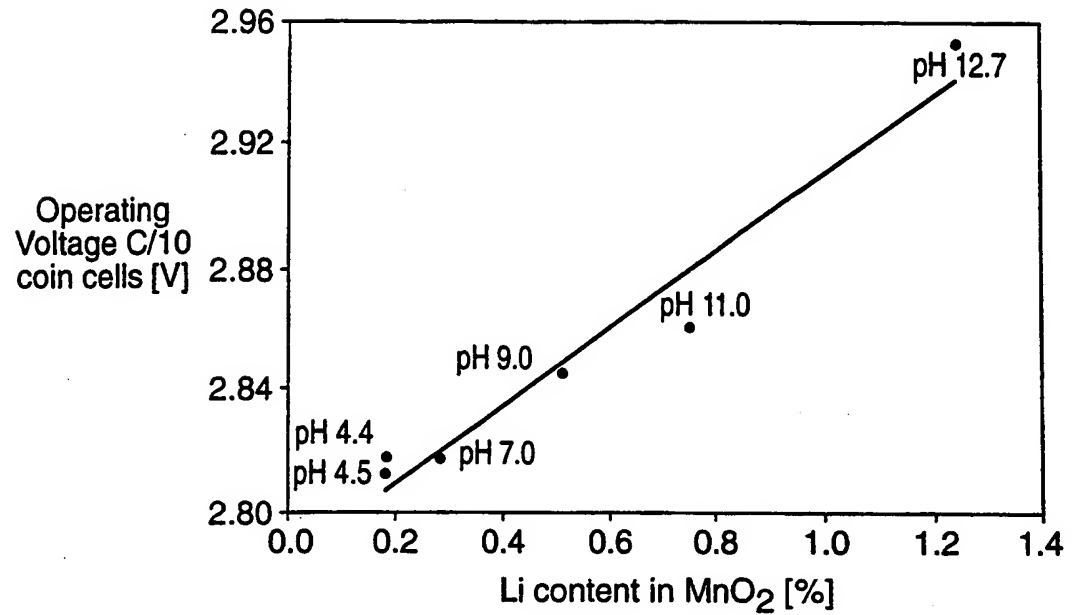
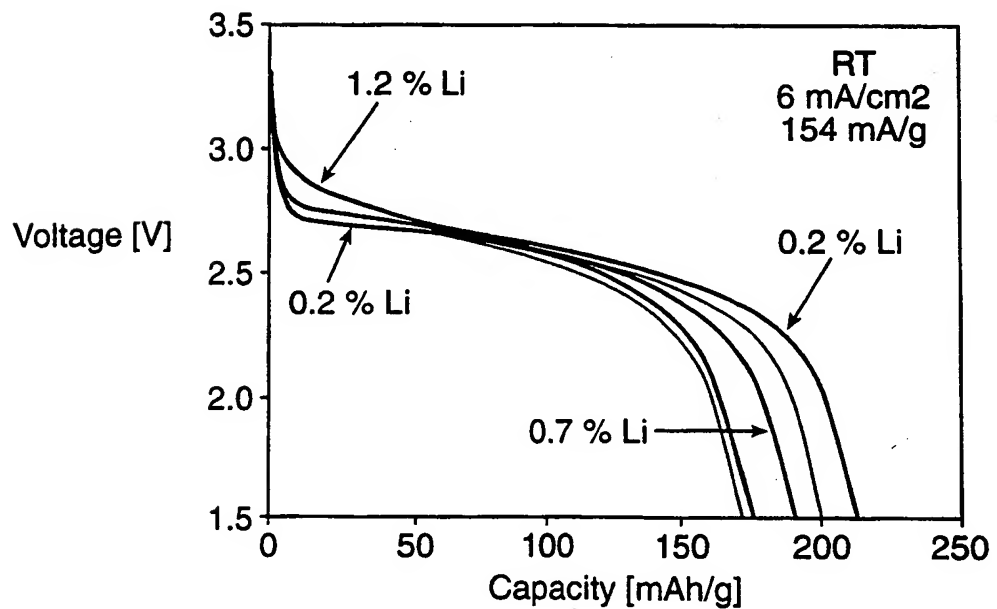
FIG. 3**FIG. 4**

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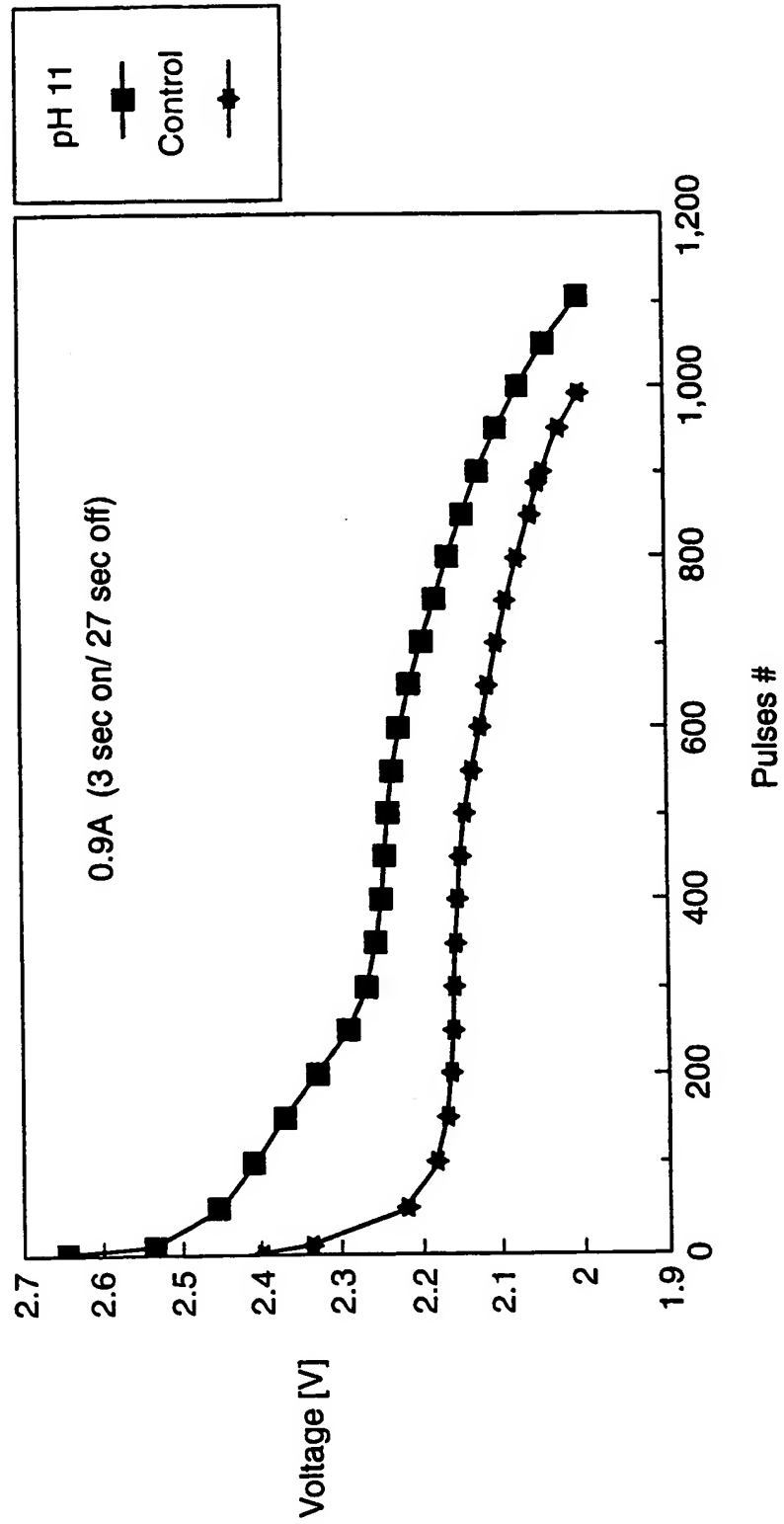
FIG. 5**FIG. 6**

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FIG. 7**FIG. 8**

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FIG. 9

INTERNATIONAL SEARCH REPORT

Int. .onal Application No

PCT/US 99/10173

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01M4/50 C01G45/02 H01M6/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01M C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	abstract	8-16, 27-36
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Y	abstract	8-16, 27-36
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

24 August 1999

Date of mailing of the international search report

31/08/1999

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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